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AUTOMATED TEST PROCEDURE FOR
THE DETERMINATION OF TRUE
COLOUR

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**AUTOMATED TEST PROCEDURE
FOR THE DETERMINATION OF
TRUE COLOUR**

**Ben Cheung
Water Quality Section
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Abstract

An automatic colourimetric procedure was developed for the measurement of colour in True Colour Units (TCU). The colour was measured via a continuous flow of supernatant from a settled sample through a colourimetric system utilizing two cells of different path lengths, and also equipped with two different broad band filters. Colour estimates obtained from sample filtrates and supernatants showed that a high degree of precision and accuracy was achieved by this automated method. The calibration is linear from 0-70 TCU, and the standard deviation for 118 duplicate analyses between the range of 10-35 TCU was 0.37 TCU. Because of this degree of precision, the maximum desirable colour of 5 TCU¹ for drinking water can be analyzed with great confidence. The recommended colour for the distribution system of a water supply in the 1962 US Public Health Service standard should not exceed 15 units on the platinum - cobalt scale².

Introduction

The revised Ontario Drinking Water Objectives³ for colour have been changed from Apparent to True Colour, and the units for this parameter are to be expressed in True Colour Units (TCU) rather than Hazen Units. These changes bring MOE in line with the Federal Department of the Environment and the Environmental Protection Agency of the United States. In support of the new objectives, the Water Quality Section initiated a project to develop an automated test procedure for the determination of true colour. In fact, this test procedure was only a modification of the spectrophotometric colour procedure⁴ developed by J. Crowther and J. Evans, 1977.

Changing the units for colour measurements does not affect the reported numerical value because both Hazen and True Colour units are based on the same platinum - cobalt standard for which one colour unit is equated to 1 mg platinum.

Apparent colour values are equivalent to True Colour measurement provided the sample contains no particulates or turbidity. If the latter are present, True Colour is normally measured on the sample filtrate⁵ or the supernatant of a centrifuged sample. Standard Methods, however, notes that a turbidity correction can be estimated by using two different filters. In developing a True Colour procedure, techniques for turbidity corrections were very attractive because filtering or centrifuging samples is labour-intensive.

Using data accumulated during a previous study of colour measurements⁴, an Auto Analyzer system, which includes a reference stream, was designed for the supernatant of settled samples. The purpose of the reference stream was to eliminate the effect of non-settleable solids on colour measurements. Broad band filters from the currently-used Klett-Summerson colourimeter were adapted to fit the holders of the Technicon AAll colourimeter. The broad band filter, with transmission limits of 405 to 450 nm, was suitable for true colour measurements while the filter with transmission limits of 660 to 740 nm, gave a turbidity/particulate only measurement. To obtain an appropriate correction for non-settleable solids at the required wave-lengths (405 to 450 nm), the path lengths of the flow cells were 3.0 cm for the colour stream and 5.0 cm for the reference stream. This imbalance in cell length was designed to handle the relationship between light scattering and wavelength: the effect of particulates on absorbance measurements increases as the wavelength decreases. Once assembled, the Auto Analyzer system was calibrated with platinum-cobalt standards and evaluated.

Experimental

1. Apparatus

- (i) Technicon Sampler
- (ii) Technicon Pump
- (iii) Voltage Stabilizer
- (iv) Technicon AAII Colourimeter
- (v) 3.0 and 5.0 cm Flow Cells
- (vi) Broad-Band Filters (405-450 nm and 660-740 nm)
- (vii) Single Pen Chart Recorder

2. Chemicals

- (i) Platinic potassium chloride, PtK_2Cl_6 , purified grade.
- (ii) Cobaltous chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, reagent grade crystals.
- (iii) Hydrochloric acid, HCl, reagent grade, concentrated.
- (iv) Platinic-cobalt colour standard, (500 TCU) BDH.

3. Calibration Standards

- (i) Stock Calibration Standard Solution - 500 Colour Units (TCU).

Dissolve 1.246 g platinic potassium chloride, PtK_2Cl_6 (equivalent to 500 mg metallic Pt) and 1.00 g crystalized cobaltous chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (equivalent to about 250 mg metallic Co) in deionized distilled water with 100 ml of concentrated Hydrochloric acid and dilute to 1.0 litre with deionized, distilled water.

(ii) Working Calibration Standards

Working calibration standards are prepared by diluting the following volumes of the stock calibration standard solution to 1.0 litre with deionized, distilled water:

<u>Volume of Stock Standard (ml)</u>	<u>Colour Concentration (TCU)</u>
4.00	2.00
10.0	5.00
50.0	25.00
100.0	50.0
150.0	75.0
175.0	87.5

4.0 QC Standard Solutions

QC-A (50 TCU): Pipette 100.0 ml BDH Platinic-cobalt colour standard (500 TCU) and dilute to 1.0 litre with distilled, deionized water.

QC-B (25 TCU): Pipette 50.0 ml BDH Platinic-cobalt colour standard and dilute to 1.0 litre with distilled, deionized water.

QC-C (5 TCU): Pipette 10.0 ml BDH Platinic-cobalt colour standard and dilute to 1.0 litre with distilled, deionized water.

LTB (Long Term Blank): Retain a supply of deionized water used to prepare the QC Solutions.

Colour Procedure

- Check tubes, which have been washed by stores, and select a clean set.
- Collect samples, cover with parafilm, and allow to stand at least one hour.
- Fill the bottle, which supplies the reservoir of sampler with deionized, distilled water (DDW).
- Empty containers which collect waste from colorimeter and sample reservoirs.
- Pump DDW through system.
 - Turn on colorimeter and chart recorder; allow to warm up - approximately 15 minutes.
 - Check sampler times: overall time is 1 min., 10 sec.; sampling time is 40 sec.
 - Set zero on chart recorder to coincide with zero on colorimeter; set full scale on chart recorder to coincide with full scale on colorimeter. The chart recorder setting will be 50 mv plus a selected position of the attenuator knob. Confirm settings by switching the colorimeter from 0 to full scale.

NOTE: ONCE THE ZERO POSITION ON THE CHART RECORDER HAS BEEN SET, DO NOT TOUCH OR CHANGE IT THROUGHOUT THE REMAINDER OF THE RUN.

- With the colourimeter on 'Normal' and with the standard cal setting at the value used for the previous run, adjust baseline knob on colourimeter to give a reading of 25 lines on the chart recorder.
- Turn setting on chart recorder to 10 mv and using the attenuator knob on the chart recorder, adjust the pen to give a reading of 100 lines (the chart recorder has now a four-fold electronic expansion of colourimeter signal).

NOTE: ONCE SET, DO NOT ADJUST ATTENUATOR KNOB OF CHART RECORDER THROUGHOUT THE REMAINDER OF THE RUN.

- Set a baseline on chart recorder to five lines using baseline knob on colorimeter.
- Run two 75 TCU standards; adjust peak height with standard cal knob to 75 lines on the second standard. Run one more 75 standard to confirm standard cal setting. Record the standard cal setting on QC data sheet.

- Run calibration standards 2, 5, 25, 50, 75 and 87.5 TCU, record values. If readings are off by more than 2 TCU, check with senior technician.
- Run QC standards: QC-A (50 TCU), QC-B (25 TCU), QC-C (5 TCU) and LTB1 (long term blank). Run first portion of three duplicates (run second portion at normal position within run). Record QC values. Confirm that A+B, A-B, B+C and B-C meet criteria.
- Analyze samples: 10 samples, blank, 10 samples, 75 TCU standard, 75 TCU standard, blank.
- If any sample is off scale (high) or noisy, filter the sample (glass fibre filter) and repeat using a dilution if necessary.
- When run is completed, convert peak heights to colour units using a strip chart.
- Record colour values for samples on bench sheet.

Results and Discussion

Calibration

The system was designed for analyzing true colour in the range of 0-87.5 TCU (True Colour Unit) without dilutions. This automated colourimetric method proved simple to set up and to operate. The calibration curve was linear over the range 0-70 TCU (Figure 1), and the resolution was 0.5 TCU or equivalent to one half of a line on the chart.

The colorimeter was calibrated with standard solutions prepared from the platinic-cobalt stock solution (500 TCU) which originally contained 10% hydrochloric acid.

At the outset of this study it was believed that the absorbance of the platinic-cobalt standard was negligible at wavelengths greater than 650 nm⁴. However, tests showed that the amount of hydrochloric acid present in the standard colour solutions showed absorbance reading on the chart. To illustrate this, two steps were taken to evaluate the magnitude of absorbance caused by an equivalent amount of acid present in the standard solutions. The colourimeter was initially zeroed with distilled water running through both cells. First, distilled water was running through the colour cell (3.0 cm with 405-450 nm filter) while colour standards of 10-80 TCU, with increments of 10 TCU, were

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running through the reference cell (5.0 cm with 660-740 nm filter). There was a gradual increase of negative absorbance as colour concentrations increased. These absorbance values were caused by the colour of the standard plus the hydrochloric acid in it. The second step was to run distilled water through the colour cell and a series of acid solutions through the reference cell; the acid levels were equivalent to those found in the colour standards. As similar results were obtained for both series of test solutions, the absorbance readings for the colour standards were due to their acid content. The average error due to colour (0-80 TCU) measured at the reference cell was negligible (0.6%) while a 2.9% difference was caused by the acid in the standards. Thus the use of a reference channel decreased measurements of sample colour by 2.9%.

Reasonably high stability and precision were obtained on the platinic-cobalt colour standards (Table I). The correlation between the theoretical and measured values for colour standards was better than 99.5%.

Precision

To establish statistical parameters for precision, duplicate aliquots of 163 Domestic Water and River and Lake samples were analyzed. The colour range was representative of colour concentrations in routine samples. The samples were allowed to stand for 24 hours so that the effect of turbidity/particulates was reduced to a minimum. The precision between the manual and automated methods

is shown in Table II. The overall standard deviation for the automated method was 0.35 TCU. Duplicate data for samples with colour less than 10 TCU was utilized to estimate the detection criterion which was 0.46 TCU (1.645S).

Intercomparison

The term "True Colour" refers to the colour of water from which turbidity and particulates have been removed. To evaluate the effectiveness of the designed reference channel, filtrates and supernatant of settled samples (104 randomly chosen River and Domestic Water samples) were analyzed by the proposed automatic method (Table III). When the data were subjected to linear regression analysis, the slope was 1.02, and the intercept was -0.17 TCU; the correlation coefficient was 0.9973.

Since the difference in slope from unity between the settled and filtered sample is small, the reference channel effectively compensated for the residual turbidity in the samples.

Effect of change on Histroical Data

Theoretically, there should be no difference in colour measurement between the manual (Klett-Summerson method) and automated (AAII method) where there is no turbidity/particulates in the samples. However, if turbidity/particulates are

present, the true colour result will be lower and the bias will increase as turbidity/particulates content increases. The correction factor for the turbidity in the automated True Colour test is 11.3% larger than that for the Apparent Colour test. (Using the Klett-Summerson filter photometers, the correction factor was $1.5 \times$ absorbance for the #69 filter. The corresponding correction factor for the automated procedure is 1.67. The latter was attained by using different cell path lengths in the sample and reference sides of the colourimeter and assumes Beers Law: $\epsilon = ABC$).

The difference between manual and automated procedures will not be excessive because an arbitrary upper limit was imposed on turbidity measurements for the Apparent Colour test: a maximum absorbance of 0.020 when the sample was measured with the #69 filter (Transmission range of 660-740 nm) and a 4.0 cm cell path. When the absorbance reading exceeded 0.020 the sample was filtered and True Colour was then reported. If a sample has the maximum allowable turbidity for an Apparent Colour test, then its true colour value will be 4.5 units lower than the Apparent Colour value. Generally, the average difference between the two procedures will be lower than this amount. To illustrate, 70 samples were analyzed by the manual procedure for Apparent Colour and by the automated procedure for True Colour (Table IV). The average difference between the two procedures was only 0.17 TCU. The standard deviation of difference over the range 0-70 TCU was 1.2 TCU.

Conclusion

The proposed automated colourimetric system for True Colour measurement is precise, quick (>50 samples/hour) and simple to operate. The mean standard deviation on routine samples of range from 0-10 TCU for the automatic procedure was 0.28 ($n=32$) against 0.39 ($n=56$) for the manual method. The proposed automatic method will increase productivity by two thirds without sacrifice of precision and accuracy and will eliminate labour-intensive procedures. The conversion of reporting "Apparent Colour" to "True Colour" will place MOE in line with the Federal Department of the Environment and Environmental Protection Agency of the United States.

The regression analyses statistics have confirmed that the difference of colour between settled and filtered sample was small (correlation = 0.9973, $n= 104$), so that colour measurements on the settled aliquots can safely be reported as TCU (True Colour Unit).

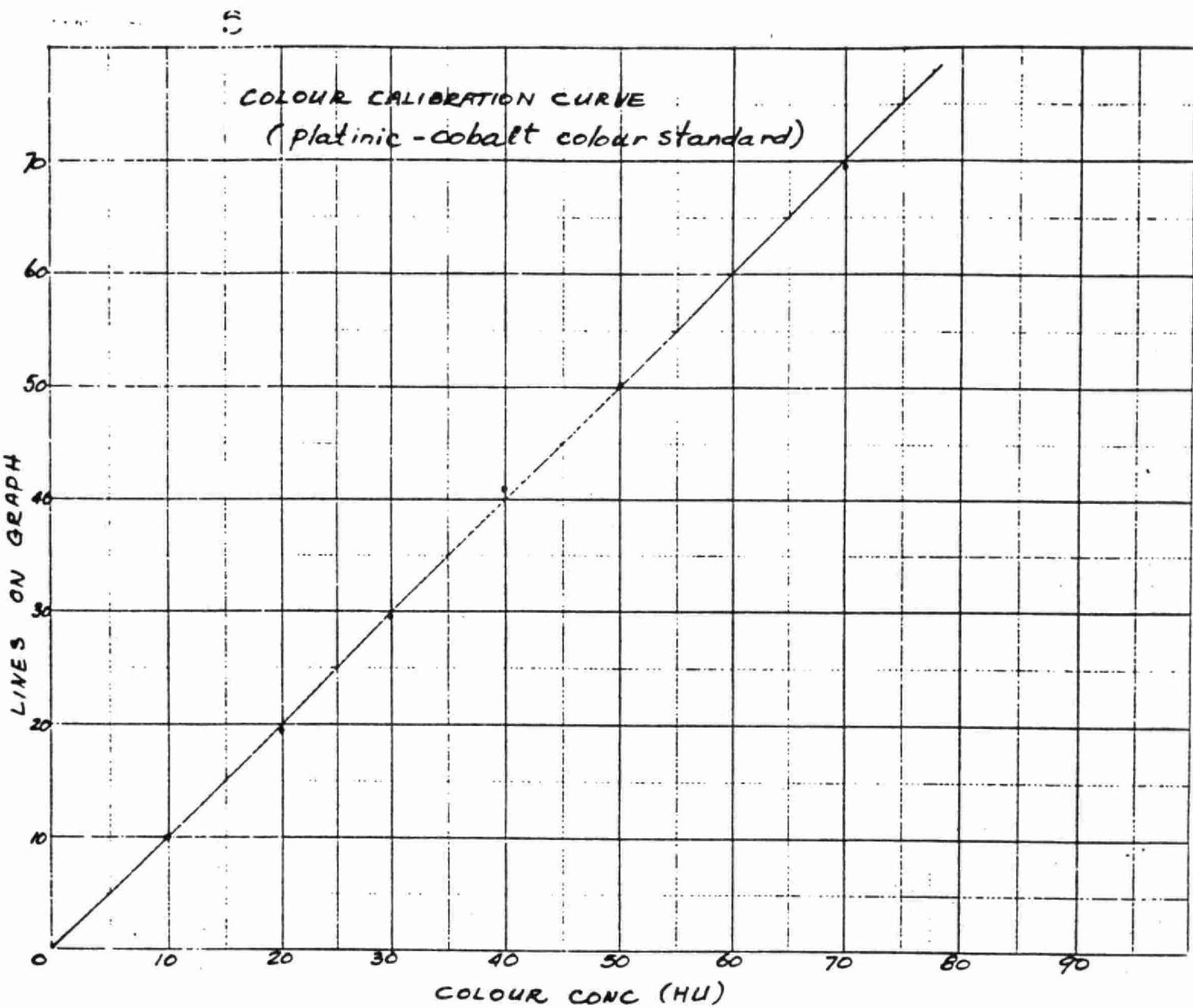


FIGURE I

TABLE I

Precision as Measured by Analysis of Replicate Colour Standards (Between Run)

Colour Standards (TCU)	True Colour - Automatic Method		
	No. Samples	Average Colour (TCU)	Standard Deviation (TCU)
5.0	12	4.88	0.24
10.0	10	10.05	0.26
30.0	11	30.61	0.82
60.0	16	59.88	1.48

TABLE II

Precision as Measured by Analysis of
Duplicate Sample Aliquots

Analytical Colour Range of Sample (HU)	Apparent Colour* by Klett-Summerson Method		True Colour by Automated AAII Method	
	No. Sample	Mean Std. Dev. (HU)	No. Sample	Mean Std. Dev. (HU)
< 10	56	0.39	32	0.28
10-35	67	1.10	118	0.37
35-70	7	0.55	13	0.34
35-70	7	0.55	13	0.34
0-70	130	0.83	163	0.35
Detection Criterion		0.64		0.46

* Data abstracted from Water Quality Performance Report, 1983.

TABLE III

Summary of Intercomparison
Between Settled and Filtered Samples

Regression Analysis:

Number of Samples	=	104
Correlation	=	0.9973
* Y on X, slope	=	1.0189
Intercept	=	-0.1695
Standard Dev. of Slope	=	0.005

* where Y = Settled

X = Filtered

TABLE IV**Average Difference Between Klett-Summerson
(manual) and AAII (automatic)**

Colour Standards (TCU)	No. Samples	Average Difference (TCU)	Standard Deviation of Differences (TCU)
0-10	16	-.32	1.2
10-35	47	+0.14	1.2
35-70	7	+1.5	1.8
0-70	70	+0.17	1.2

Regression Analysis:

Number of Samples = 70
Correlation = 0.9823
* Y on X, slope = 0.9479
Intercept = 0.7764

* where Y = Klett-Summerson

X = AAII

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